

## Behaviour of Environmental Plutonium at very Low Concentration

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(Received October 25, 1991; revised February 10, 1992)

*Environmental Pu / Disproportionation of Pu(V) /  
Kinetics / Sub-tracer scale*

### Abstract

Plutonium is widely distributed in environmental systems at very low concentrations and can undergo complexation and disproportionation reactions. At these concentration levels, the validity of the law of mass action for describing the equilibrium state of the reactions may be questioned. Specific cases, such as complexation of Pu, and disproportionation of Pu(V) at the sub-tracer scale are discussed. Speculations about the completion of reactions involving less than 100 Pu atoms are developed.

### 1. Introduction

Despite the relatively large amounts (about 4.2 tons) of anthropogenic plutonium released into the environment [1, 2], the steady-state concentration of the element in aquatic systems is low and remarkably constant [1, 3-11]. For instance, average plutonium concentrations in lake waters are in the 0.1 to 0.5 fCi/l range (1 fCi =  $3.7 \times 10^{-5}$  Bq), lake sediments contain about 100 fCi/g. In ocean waters the concentration is of the order of 1 fCi/l and in sea sediments about 5 fCi/g.

Fall-out plutonium is characterized by the isotope ratio  $N(^{240}\text{Pu})/N(^{239}\text{Pu}) = 0.18$ . One fCi of this plutonium corresponds to  $2.8 \times 10^7$  atoms or  $4 \times 10^{-17}$  mol.

In soils, most of the plutonium is concentrated in the first 10 cm of depth, with a concentration above 5 fCi/g. A typical value of the distribution coefficient,  $K_d$ , of Pu between soils and ground waters is  $10^4 \text{ cm}^3/\text{g}$ . Accordingly, the amount of Pu at equilibrium in stagnant ground waters is less than  $10^5$  atoms per  $\text{cm}^3$ . This value is a representative average of the Pu concentration, although the latter may be locally much higher.

The oxidation state of Pu in the geosphere and biosphere is fairly well known [4, 12-13]. Quite generally, the oxidation states Pu(IV) and Pu(III) are encountered in solid materials and the higher valencies Pu(V) and Pu(VI) predominate in natural waters. In living organisms the concentration is less than  $10^5$  atoms/ $\text{cm}^3$ , but probably with a non-uniform distribution.

Natural plutonium has its origin in the reactions of neutrons with  $^{238}\text{U}$  in uraniferous minerals and

rocks. These reactions have proceeded over geological times and the steady-state ratio  $^{239}\text{Pu}/^{238}\text{U}$  is about  $10^{-12}$  [7]. This figure is equivalent to a few thousand atoms of  $^{239}\text{Pu}$  per gram of rock containing 1 ppm of uranium. Highly diluted Pu solutions may result from the percolation of water through the rocks. In this way, ground and underground waters may contain a limited number of atoms of Pu which will depend on many parameters, such as the uranium content of the media, the leaching process, the solubility of Pu, etc.

Finally, very small pockets of fluids occupying a volume of tens of cubic microns up to several cubic millimeters, may exist in rocks and serve as traps for natural Pu atoms.

The distribution of environmental Pu in expanded aqueous systems such as lakes and oceans is relevant to tracer scale chemistry. The molar concentration of dissolved Pu in these natural reservoirs is of the order of  $10^{-17} \pm 1$ . The behaviour of Pu at this scale can be fairly well predicted by applying classical thermodynamic and kinetic concepts [14].

On the other hand, in certain natural systems of limited extent, the expected concentrations of Pu are so low that they correspond to a "sub-tracer" level for which these usual concepts no longer hold.

In the present work, the expected behaviour of tracer and sub-tracer scale Pu in environment-like aquatic systems will be discussed.

### 2. Prognosis of Pu reactions in the environment

The conditions under which various thermodynamically stable Pu species can exist and coexist can be inferred from Eh-pH diagrams. The latter are established for specific sets of parameters such as the nature and concentration of complexing agents present in the system.

The Pourbaix diagram represented in Fig. 1 assumes that the Pu species form true solutions and that no solid phase is present. More precisely, one excludes here the formation of a solid carrier which could incorporate Pu by some coprecipitation process, or the formation of radiocolloids or the sorption of Pu on colloidal particles such as polysilicic acids, iron hydroxides or clay particulates. These processes are generally not reversible and hence their occurrence cannot be predicted from thermodynamics.



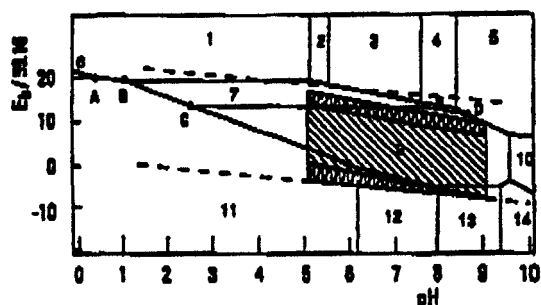


Fig. 1. Eh-pH diagram for Pu species and  $\log P(\text{CO}_2) = -2$ , drawn with data from Table 2. Disproportionation reactions occur at points A, B, C and D with the following equilibria:

- A)  $3\text{Pu(IV)} \rightleftharpoons 2\text{Pu(III)} + \text{Pu(VI)}$   
 B)  $3\text{Pu(V)} \rightleftharpoons \text{Pu(III)} + 2\text{Pu(VI)}$   
 C)  $2\text{Pu(IV)} \rightleftharpoons \text{Pu(III)} + \text{Pu(V)}$   
 D)  $3\text{Pu(V)} \rightleftharpoons \text{Pu(IV)} + \text{Pu(VI)}$

The four oxidation states coexist along the segment AB. The window delineates the Eh-pH characteristics of most natural waters. The doubly-shaded areas represent the uncertainty in the window borders. Numbers in the diagram indicate the Pu species:

1.  $\text{PuO}_2^+$ ; 2.  $\text{PuO}_2\text{OH}^+$ ; 3.  $\text{PuO}_2\text{CO}_3$ ; 4.  $\text{PuO}_2(\text{CO}_3)^-$ ; 5.  $\text{PuO}_2(\text{CO}_3)_2^{2-}$ ; 6.  $\text{Pu}^{4+}$ ; 7.  $\text{PuO}_2^+$ ; 8.  $\text{PuO}_2\text{CO}_3$ ; 9.  $\text{Pu(OH)}_4$ ; 10.  $\text{Pu(CO}_3)_2^{2-}$ ; 11.  $\text{Pu}^{3+}$ ; 12.  $\text{PuCO}_3$ ; 13.  $\text{Pu(CO}_3)_2^-$ ; 14.  $\text{Pu(CO}_3)_3^{3-}$ .

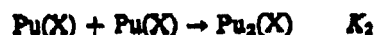
The diagram also includes the "water window" [15–17], which is the envelope corresponding to the range of Eh-pH conditions found in natural environments. Only occasional values fall outside this domain. It is seen that under oxic conditions, the only possible reaction is the disproportionation of Pu(V). The discussion will therefore be focused on this reaction, and on the competing association (limited to the first step, i.e. the formation of dimers) and complexation reactions of Pu(IV), Pu(V) and Pu(VI). In the present context, the oxidation state Pu(III) is only of minor importance, but for the sake of completeness data relative to this state will also be reported.

The three types of reactions of interest are:

- (a): Complexation of Pu in a given oxidation state, denoted by Pu(X), with ligands such as  $\text{CO}_3^{2-}$  indicated by L:



- (b): Dimerisation of Pu in a given oxidation state



- (c): Disproportionation



Another approach towards the prediction of the behaviour of Pu involves calculation of the equilibrium constants required for measurement of the equilibrium concentrations of the various Pu species. This necessary condition can be expressed by a given percentage (say, between 5% and 95%) of the total Pu concentration which should be found in the species

Table 1.  $K$  values required for the observation of possible Pu equilibria

| Reaction   | $\log K^*$ |  |
|--|------------|--|
| $\text{Pu(X)} + 1\text{L}$<br>$\rightarrow \text{Pu(X)L}_1$    | 1.3        | $-\log [L] \text{ (a)}$ $-1.27 - \log [L] \text{ (b)}$                     |
| $\text{Pu(X)} + \text{Pu(X)}$<br>$\rightarrow \text{Pu(X)}_2$  | 2.58       | $-\log C_{\text{Pu}} \text{ (a)}$ $-1.25 - \log C_{\text{Pu}} \text{ (b)}$ |
| $2\text{Pu(V)} \rightarrow \text{Pu(IV)}$<br>$+ \text{Pu(VI)}$ | 1.95       | (c) $-3.16 \text{ (d)}$  |

\* For instance  $K = [\text{Pu(IV)}][\text{Pu(VI)}]/[\text{Pu(V)}]^2$

(a)  $[\text{Pu(X)}] = 5 \times 10^{-3} C_{\text{Pu}}$ , (b)  $[\text{Pu(X)}] = 0.95 C_{\text{Pu}}$ ,

(c)  $[\text{Pu(V)}] = 5 \times 10^{-3} C_{\text{Pu}}$ , (d)  $[\text{Pu(V)}] = 0.95 C_{\text{Pu}}$

$C_{\text{Pu}}$  is the total Pu concentration

such that measurement can be performed. Calculated  $K$  values, summarized in Table 1, are then compared with those estimated as a function of pH for various concentrations of inorganic and organic complexing agents. It should be pointed out that  $K$  values for acid-base reactions in aqueous solutions such as (a) and (b) are not as easily predicted as those for redox reactions such as (c).

## 2.1 Disproportionation of Pu(V) and complexation with inorganic ligands

The principal and most common complexing agents of actinides in natural waters are carbonate anions. The carbonate concentration is expressed in terms of the  $\text{CO}_2$  pressure  $P$ , or of  $\log P(\text{CO}_2)$ . For granitic waters,  $\log P(\text{CO}_2)$  is in the range of  $-3.5$  to  $-1$  or even higher. Hence the Eh-pH diagram in Figure 1 has been drawn for an average value  $\log P(\text{CO}_2) = -2$ . The data used in setting up the diagram are summarized in Table 2, most of the values are quite recent and agree with those found in various literature surveys [8, 24–26]. The values have been adjusted to zero ionic strength with the aid of the specific theory of ionic interaction. Some of the data for Pu were obtained by extrapolating those from neighboring actinides in the appropriate oxidation state.

The scheme gives a fair picture of possible hydrolysis and complexation reactions with carbonate that Pu(III), Pu(V) and Pu(VI) aquo ions may undergo at tracer scale concentrations in aquatic systems at a pH up to 9. The formation of hydroxo-carbonate complexes has not been considered.

The prognosis is more difficult for Pu(IV) aquo ions because of the large uncertainty – several orders of magnitude – on the formation constant of  $\text{Pu(OH)}_4$ . Published data on the hydrolysis of  $\text{M}^{4+}$  actinides are reproduced in Table 3. The hydrolysis of  $\text{M}^{4+}$  ions, and particularly of  $\text{Pu}^{4+}$ , has been taken into account using a  $\log \beta_4$  value between  $-5$  and  $-9$  at zero ionic strength. The upper limit [21] is close to the more reliable  $\log \beta_4$  values determined for  $\text{M}^{4+}$  actinide ions other than  $\text{Pu}^{4+}$ . With increasing pH of the solution, Pu(IV) can be oxidized, or, alternatively, it may dis-

Table 2. Thermodynamic data corrected to zero ionic strength

| Pu aquo ion         | $E(N+1/N)$<br>mV   | Hydrolysis <sup>a</sup> |                  |                  |                  | Carbonate complexation |                   |                   |
|---------------------|--------------------|-------------------------|------------------|------------------|------------------|------------------------|-------------------|-------------------|
|                     |                    | $\log^* \beta_1$        | $\log^* \beta_2$ | $\log^* \beta_3$ | $\log^* \beta_4$ | $\log \beta_1$         | $\log \beta_2$    | $\log \beta_3$    |
| $\text{Pu}^{3+}$    | 1.015 <sup>a</sup> | -6.6                    | -14              | -25.8            |                  | 7.7 <sup>d</sup>       | 11.9 <sup>d</sup> | 13.3 <sup>e</sup> |
| $\text{Pu}^{4+}$    | 0.996 <sup>a</sup> |                         |                  |                  | -5 to -9         |                        |                   |                   |
| $\text{PuO}_2^+$    | 0.954 <sup>a</sup> | -9.6                    |                  |                  |                  | 4.7 <sup>a</sup>       | 6.2 <sup>a</sup>  | 5.3 <sup>a</sup>  |
| $\text{PuO}_2^{2+}$ |                    | -5.2                    | -12              | -20              |                  | 9.3 <sup>f</sup>       | 14.2 <sup>f</sup> | 17.4 <sup>f</sup> |

<sup>a</sup>  $\beta_n$  for  $\text{M}^{3+} + n\text{H}_2\text{O} \rightleftharpoons \text{M}(\text{OH})_n^{3-n} + n\text{H}^+$ ;  $\beta_n$  for  $\text{M}^{4+} + n\text{CO}_3^{2-} \rightleftharpoons \text{M}(\text{CO}_3)_n^{4-2n}$

<sup>a</sup> [18, 19]; <sup>b</sup> [20]; <sup>c</sup> [21] except for the lowest value of  $\log^* \beta_4$  for  $\text{Pu}^{4+}$ , see Table 3 and text, <sup>d</sup> [22] Value for  $\text{Am}^{3+}$ , <sup>e</sup> [23] Value for  $\text{NpO}_2^+$ ; <sup>f</sup> [23].  $\log \beta_3 = 40$  for  $\text{Pu}^{4+}$ .

Table 3. Fourth hydrolysis constants for  $\text{M}^{4+}$ 

| $\mu$ | $\log \beta_4$ | References and comments                            |
|-------|----------------|--|
| Pu 1  | -10.80         | [22] Recalculated from experimental data           |
| Pu 1  | -12.7          | [8] Cited as a result in [28]                      |
| Pu 0  | $-9.5 \pm 0.2$ | [29] Calculated from data in [27]                  |
| Pu 0  | $-9.5 \pm 1.2$ | [25] Selected from [29] and [30]                   |
| Pu 0  | $-9 \pm 4$     | [31] Calculated taking into account [29] and other |
| Pu 0  | -9.5           | [7, 26] Selected from [12, 17, 29]                 |
| U 0   | -5.13          | [32] SKB data base cited in [23] as personal comm. |
| U 0   | -10.3          | [29]   |
| Th 3  | -11            | [22] Cited as a personal comm. from Grenthe        |
| Th 0  | -5.5           | [33]   |
| Th 2  | -15.9 or       | [29]   |
| Th 0  | -17.4          | [29]   |

Data transformed, if necessary, with  $\log K_w = -14$  Pu data are also quoted in [48]

proportionate or precipitate as  $\text{Pu}(\text{OH})_4$ . These reactions mask the actual hydrolysis reactions of  $\text{Pu}^{4+}$ . Choosing  $\log \beta_4 = -5$  leads to a satisfactory fit of the data with respect to the solubility of  $\text{Pu}(\text{OH})_4$  and the disproportionation of  $\text{Pu}^{4+}$ . At pH greater than 9, the data are less reliable, but natural waters with this degree of alkalinity are rather scarce.

Uncertainty regarding the hydrolytic behaviour of  $\text{Pu}(\text{IV})$  is reflected in the disparity of the predicted stability regions of the Pu oxidation states [2]. In fact, the boundaries are not as sharp as Fig. 1 (drawn with  $\log \beta_4 = -5$ ) might suggest owing to the lack of precision on other data.

Part A of Fig. 2 represents the variations of  $\log K$  of the disproportionation reaction (c) with the pH for  $\log P(\text{CO}_2) = -2$ . The boundaries of the shaded areas correspond to  $\log \beta_4$  values of  $\text{Pu}(\text{IV})$  equal to -5 and -9. It is seen that the disproportionation of  $\text{Pu}(\text{V})$  is possible at pH above 7 and that in this range the  $K$  value of the equilibrium can be measured. The same

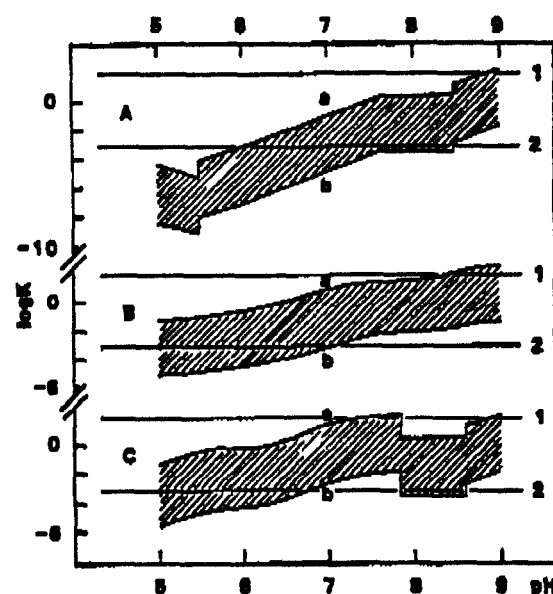


Fig. 2. Variation with pH of  $\log K$  for the disproportionation reaction of  $\text{Pu}(\text{V})$

a calculated values with  $\log^* \beta_4 = -5$  (see text)

b calculated values with  $\log^* \beta_4 = -9$ .

Lines 1 and 2 represent limits for which the reactions may be observed (Table 1).

A in the presence of carbonate anions and  $\log P(\text{CO}_2) = -2$ . The Pu species are those given in Fig. 1

B in the presence of 1 mg/l of a typical purified humic acid H.A. The species in the various Pu oxidation states are

$\text{Pu}(\text{IV}), \text{Pu}(\text{OH})_4, \text{Pu}(\text{V}), \text{PuO}_2^+, \text{Pu}(\text{VI}), \text{PuO}_2\text{A}^+$

C in the presence of carbonate anions,  $\log P(\text{CO}_2) = -2$  and 1 mg/l of humic acid. The Pu species in the various oxidation states are

$\text{Pu}(\text{IV}), \text{Pu}(\text{OH})_4, \text{Pu}(\text{V}), \text{PuO}_2^+$  up to pH = 8, then  $\text{PuO}_2\text{CO}_3^-$ ,  $\text{Pu}(\text{VI})$ , up to pH 7.8,  $\text{PuO}_2\text{A}^+$ , up to pH 8.6  $\text{PuO}_2(\text{CO}_3)_2^-$ , then  $\text{PuO}_2(\text{CO}_3)_3^{3-}$

conclusion holds for higher  $P(\text{CO}_2)$  values, but not for lower ones

The presence of other inorganic complexing anions such as  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{F}^-$  and  $\text{Cl}^-$  in sufficiently high

Table 4. Complexation of Pu species by humic acid

| pH             | $\alpha^a$ | $pK_a^b$ | Pu(III)          |                  | Pu(VI)           |                  |
|----------------|------------|----------|------------------|------------------|------------------|------------------|
|                |            |          | $\log \beta_1^c$ | $\log \beta_2^c$ | $\log \beta_1^d$ | $\log \beta_2^d$ |
| 5              | 0.6        | 4.8      | 10               | 13.58            | 7.88             | 11.2             |
| 6              | 0.8        | 5.4      | 12.22            | 14.64            | 8.84             | 12.1             |
| 7              | 0.92       | 5.9      | 13.85            | 15.43            | 9.56             | 12.75            |
| 8 <sup>e</sup> | 0.97       | 6.5      | 14               | 15.34            | 9.65             | 12.86            |
| 9 <sup>e</sup> | 1          | 6.5      | 14.4             | 15.7             | 9.8              | 13               |

<sup>a</sup> Degree of dissociation of humic acid.<sup>b</sup>  $pK_a = \text{pH} - \log \alpha / (1 - \alpha)$  [35].<sup>c</sup> Deduced from Am(III)  $\log \beta_1 = 3.5 + 10.9 \alpha$ ,  $\log \beta_2 = 10.4 + 5.3 \alpha$  [15].<sup>d</sup> Deduced from U(VI)  $\log \beta_1 = 5.0 + 4.8 \alpha$ ,  $\log \beta_2 = 8.5 + 4.5 \alpha$  [15].<sup>e</sup> For pH > 7, values extrapolated from experimental data in Ref. [15].<sup>f</sup> Neglecting reduction by humic acid.Other typical values are:  $\text{PuO}_2^+$ ,  $\log \beta_1 = 2$  to 3 (by analogy with  $\text{NpO}_2^+$ ) [36],  $\text{Pu}^{4+}$ ,  $\log \beta_1 = 9.8 + 9 \alpha$ ,  $\log \beta_2 = 16 + 9 \alpha$  [15],  $\text{Pu}^{3+}$ ,  $\log \beta_1 = 3.11$  [37].

Other values for actinides in Ref [24].

concentrations could possibly alter the present conclusions. In fact, however, the amount of these anions in water is generally too small to allow any serious competition with complexation by carbonate ions in the pH range considered.

## 2.2. Disproportionation of Pu(V) and complexation with natural organic materials

Significant amounts of organic carbon are found in natural waters in the form of soluble monomeric species of polyelectrolytes such as humic compounds, together with suspended solid matter [15, 34]. The influence of this organic matter on the behaviour of Pu has been recognized for a long time; it appears very complicated and with presently available data, adequate modelling of the phenomena has not yet been developed.

However, it has been observed that only the humic acids can act as complexing agents of Pu, presumably because of their carboxylic acid groups [15]. These substances may play a prominent role in the solution chemistry of Pu, even in the presence of carbonate anions. For Pu(IV), at pH > 9, the hydrolysis prevails over the complexation by carbonate. Pu(V) is more easily complexed by carbonate ions than by humic acids, and carbonate competes with humic acids for the complexation of Pu(VI). Finally, the higher oxidation states may be reduced by the action of reducing functional groups of the organic matter.

On the basis of these qualitative trends and from data given in Table 4, the variation of  $\log K$  for reaction (c) as a function of pH has been tentatively represented for a concentration of humic acid HA of 1 mg/l. The theoretical capacity in COOH groups of this acid is taken as 5 meq/g. Assuming that organic

complexation of  $\text{PuO}_2^+$  prevails over hydrolysis, the dominant species is  $\text{PuO}_2\text{A}^+$  over the whole pH range of interest. The possible reduction of Pu(VI) by the humic acid has been neglected, especially since data on redox reactions are frequently lacking [15].

The computed  $\log K/\text{pH}$  variation is shown in Fig 2, part B. The concordance of the estimated  $K$  values with those required for the observation of equilibrium suggests that, within some range of pH, Pu(V) may undergo a simple disproportionation in the presence of humic acid.

## 2.3. Disproportionation of Pu(V) and complexation by inorganic and organic anions

If both types of complexing species intervene, the behaviour of Pu may become very complicated. Part C of Fig 2 shows the variation of  $\log K$  as a function of pH for reaction (c), with the same concentration of humic acid. The conclusions with respect to the disproportionation of Pu(V) are not very different from those found in the previous case.

In summary, the variations of  $\log K$  as a function of pH reported in Fig 2 are tentative and should be interpreted with caution. However, it appears that the complexation of Pu by humic acids and carbonate anions may be favoured in certain aquatic systems and that, under favourable conditions, self-redox reactions of Pu may occur, provided that the latter are not kinetically hindered. This is of considerable importance and will be discussed below.

## 3. Completion of prognosticated Pu reactions

Some aspects of the kinetics of reactions between microcomponents, such as the Pu species considered here, have been discussed recently [14]. The reactions involve at least one second-order rate-controlling step with respect to two microcomponents; in these circumstances the time required to achieve equilibrium may be very long. Knowledge of this time is generally not easily accessible, owing to lack of relevant kinetic data, which are by far less available than thermodynamical ones. For this reason, it is necessary to make crude extrapolations.

Let us consider a reaction between two microcomponents  $E_1$  and  $E_2$ , controlled by a second-order step process with a rate constant  $k$  ( $\text{M s}^{-1}$ ). Whatever the initial concentrations of  $E_1$  and  $E_2$  at the Pu tracer level, the half-time  $\tau$  (s) of the reaction is given approximately by

$$\tau = 1/kC$$

in which  $C$  is the total Pu concentration. If the number  $N$  of atoms of the microcomponent is contained in a volume  $V$  (L), it follows that

$$\log \tau = 23.7 + \log V - \log N - \log k$$

For the fastest known reactions,  $k = 10^{11} \text{ M s}^{-1}$ . Assuming  $N = 10^2$  and for a volume within the limits  $1 \mu\text{m}^3$  and  $1 \text{ cm}^3$ , one finds

$$50 \mu\text{s} < \tau < 1.6 \text{ y}$$

A decrease in the rate constant  $k$  would yield much higher reaction times. Conversely, if the half-time of the reaction is assumed to be  $\tau = 10^3 \text{ y}$ , the corresponding  $k$  values would be comprised between  $10$  and  $10^8$  for the same limits of volume. The reaction hindrance increases with the spatial extension of the system containing the microcomponents. This point has important implications in environmental reservoirs.

Most of the known data on the kinetics of redox or self-redox reactions of Pu refer to aquo ions [38–41]. It has been shown that the reaction mechanisms are very complicated. The reaction rate depends *inter alia* on the initial composition, pH, rupture and formation of Pu-oxygen bonds, and complexation of the aquo ions. The rate increases with decreasing pH when Pu–O bonds are broken and increases with the pH when the Pu–O bonds are formed. It also increases with the complexation of Pu. The disproportionation of  $\text{PuO}_2^+$  has been reported to be fast at  $\text{pH} < 1.7$  and  $\text{pH} > 7$ , but it takes several days at  $\text{pH} 3.5$ .

Kinetic data on the dimerisation and complexation of Pu which would be helpful in the present context are lacking. However, it may be assumed that the condensation of hydrolyzed species by formation of oxo bonds should be faster at higher pH owing to the increasing number of OH groups.

These data point to the possible completion over geological time scales of the equilibria discussed above, in particular in closed natural systems with a limited spatial extension.

#### 4. Behaviour of a population of few Pu atoms

It has been shown [42–44] that the law of mass action, expressed in terms of the number of reacting entities (atoms, molecules, ions) is inadequate for description of the equilibrium state of a system which contains only a very limited number of entities, i.e., below a few hundred. Instead, the *average* number  $N_E$  of the reacting entities  $E_i$  must be used. The latter is calculated from the canonic probability  $P$  for realizing the microstates of the system, set up in terms of the exact, but strictly limited, values  $N_{Ei}$ :

$$N_E = \sum P N_{Ei}$$

The summation is performed over all possible discrete values of  $N_{Ei}$ . This non-classical treatment has been developed because under such conditions the Stirling approximation no longer applies and the concept of chemical potential cannot be used. With increasing number  $N_E$  of the reacting entities, the equilibrium constant  $K$  computed with the average populations tends toward equality with the constant calculated in the classical way. Hence the peculiar behaviour

of the limited number of reacting entities can be expressed by the ratio

$$q = \frac{K}{N_E}$$

which becomes equal to unity when the classical description applies.

This treatment has been applied to various reactions of Pu. The calculation shows that for all reactions between a microcomponent, such as Pu, and a macrocomponent, for instance a complexing agent like  $L$  in reaction (a),  $q = 1$ , provided all stoichiometric coefficients of the microcomponent are equal to one. This conclusion holds for any number of reacting entities. Accordingly, the behaviour of a few Pu atoms with respect to complexation with a macroscopic amount of reagent is, on the average, the same as at the tracer scale.

On the other hand, for reactions between two microcomponents, such as the dimerisation reaction (b) and the disproportionation (c), the ratio  $q$  is a function of the number of reacting entities and must be calculated for each specific equilibrium.

For illustration, two extreme situations will be considered: first, the evolution of  $q$  for the equilibria (b) and (c) when the number of Pu atoms in a given oxidation state increases (starting with 2 atoms) and for which equilibrium may be achieved only in a very distant future. The second case refers to the last steps in the existence of a population of Pu atoms before their total extinction, assuming that at that moment the equilibrium state (for instance that of the disproportionation reaction (c)) has been established.

#### 4.1 Progressive growth of the number of Pu atoms

The variation of the ratio  $q$  for reaction (b) as a function of the number of  $\text{Pu(X)}$  entities is shown in Fig. 3 for the two values  $10^{-2}$  and  $10^2$  of the "classical" equilibrium constant  $K$ . When  $K < 1$  and the number of Pu atoms is below a few tens, the extent of dimerisation is less than at "usual" tracer concentrations. If  $K > 1$ , the evolution is more complicated because the extent of reaction may be higher or lower than that expected for a large population (above several hundred entities). This arises from the fact that  $q$  depends on the number of  $\text{Pu(X)}$  entities, which is equal to that of the Pu atoms; the latter may be even (for 2 modulo 2) or odd (3 modulo 2). For each additional Pu atom, the system fluctuates from one group to the next and the reaction proceeds chaotically until the population has reached several hundred entities.

At this point of the discussion, it is interesting to note that the adsorption (supposed reversible) of a Pu species on some colloidal form of an element M according to



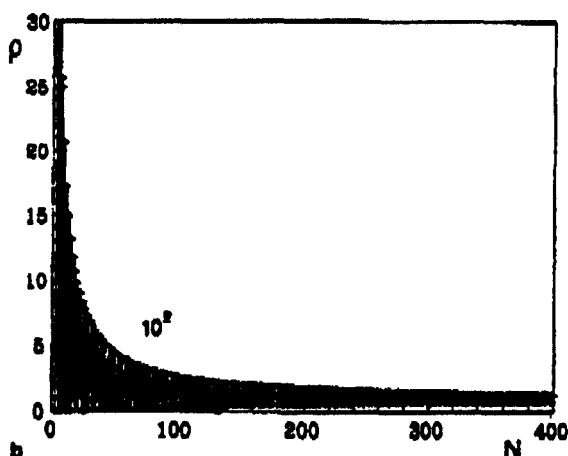
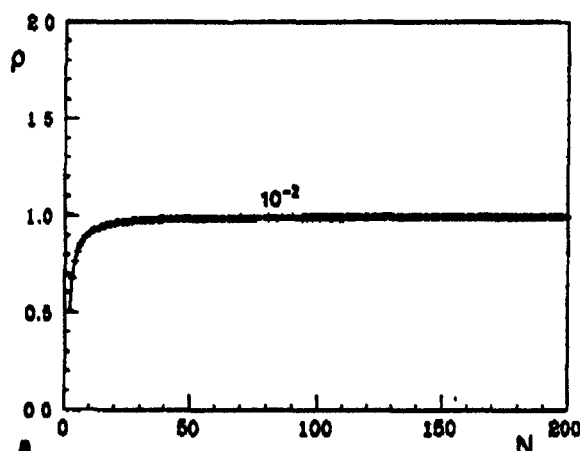


Fig. 3. Equilibrium  $\text{Pu(X)} + \text{Pu(X)} \rightarrow \text{Pu}_2\text{(X)}$ , constant  $K_2$ . Variation of the ratio

$$\rho = \frac{N_{\text{Pu(X)}}}{N_{\text{Pu}_2\text{(X)}}} \frac{1}{K_2}$$

with the initial number  $N$  of  $\text{Pu(X)}$  entities; the initial number of  $\text{Pu}_2\text{(X)}$  is zero

3a:  $K_2 = 10^{-2}$

3b:  $K_2 = 10^2$ . The curve separates into two branches; for the upper branch,  $N=2$  modulo 2, and for the lower one,  $N=3$  modulo 2. The first  $N, \rho$  values written  $N/\rho$  are the following: 2/100, 3/0.009, 4/50, 5/0.019, 6/33, 7/0.029, 8/25, 9/0.038 and 10/20.

is formally similar to reaction (b). But to describe the fixation process, one must consider the case in which the initial number of colloids  $\text{Coll(M)}_0$  exceeds that of the  $\text{Pu(X)}$  entities. It is found that when  $\text{Coll(M)}_0$  increases,  $\rho$  rapidly attains its limiting value of 1 and the chaotic phase ceases. The behaviour of  $\text{Pu}$  is very sensitive to the initial number of colloidal adsorption centers. The reverse of reaction (b) has been discussed earlier [44].

The behaviour of  $\text{Pu}$  with respect to disproportionation reaction (c) is shown in Fig 4, which represents variations of  $\rho$  as a function of the number of  $\text{Pu(V)}$  entities for selected values of  $K$  and the simple initial condition  $N(\text{Pu(IV)})_0 = N(\text{Pu(VI)})_0 = 0$ . For  $K$  values  $\ll 1$  and when the number of  $\text{Pu(V)}$  atoms is

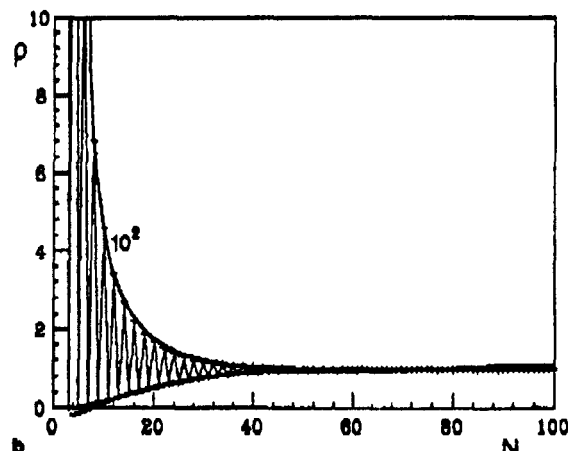
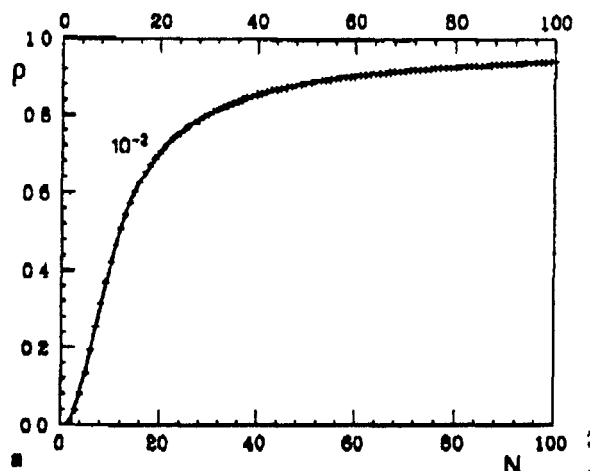


Fig. 4. Equilibrium  $2\text{Pu(V)} \rightarrow \text{Pu(IV)} + \text{Pu(VI)}$ , constant  $K$ . Variation of the ratio

$$\rho = \frac{N_{\text{Pu(V)}} N_{\text{Pu(VI)}}}{N_{\text{Pu(IV)}}^2} \frac{1}{K}$$

with the initial number of  $\text{Pu(V)}$  entities. The initial number of  $\text{Pu(IV)}$  and  $\text{Pu(VI)}$  is zero

4a:  $K = 10^{-2}$

4b:  $K = 10^2$ . For the upper branch,  $N=2$  modulo 2, for the lower branch,  $N=3$  modulo 2. The first  $N, \rho$  values are 2/100, 4/25, 6/12.5

less than about 100, disproportionation is less advanced than at the tracer scale or at higher concentrations under conditions for which equilibrium is established. Under the same conditions but with  $K=1$  or  $K>1$ , the behaviour is again chaotic, as in the preceding case. The case of the reverse remutation reaction has been discussed in Ref [44].

#### 4.2 Progressive death of a population of $\text{Pu}$ atoms

Assuming that the disproportionation equilibrium (c) is established at the tracer scale, i.e. for a large number of  $\text{Pu}$  atoms, progressive radioactive decay will lead

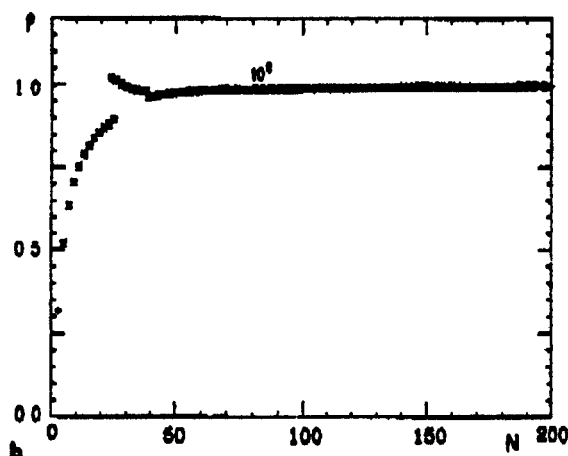
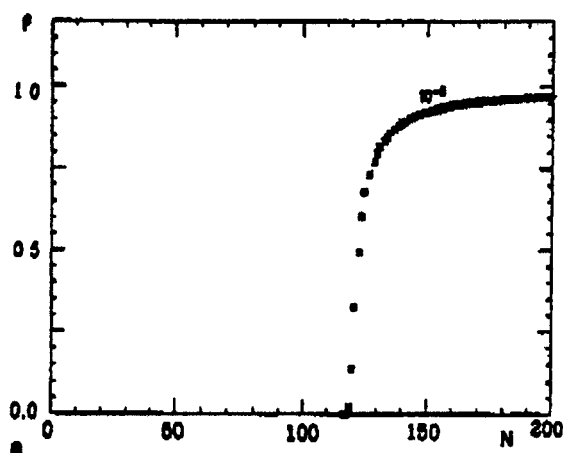


Fig. 5. Same equilibrium as in Fig. 4. The initial numbers  $N_0$  of Pu(IV), Pu(V) and Pu(VI) are the equilibrium concentrations. The  $N$  values are those allowed by the stoichiometric coefficients, starting from  $N_0$  even = 200 (symbol +) or  $N_0$  odd = 201 (symbol \*)

5a:  $K = 10^{-2}$

5b:  $K = 10^{-1}$

to sub-tracer conditions when  $N(\text{Pu})$  is less than a few hundred, and eventually the system will become extinct. Since  $N$  decreases slowly, it may be considered that the equilibrium is restored after each decay step. In this case, the initial numbers of the three entities at each stage are equal to those prevailing in the previous equilibrium, and are determined by the successive values of  $K$  and  $N$ , i.e.:

$$N_{\text{Pu(V)}} = \frac{N}{1+2\sqrt{K}} \quad N_{\text{Pu(IV)}} = N_{\text{Pu(V)}} = N_{\text{Pu(VI)}} \sqrt{K}.$$

The variation of  $q$  as a function of stoichiometrically allowed values of  $N$  is shown in Fig. 5. Computation of the ratios  $q$  is carried out according to the following sequence, starting with a given set of values for  $N$  and  $K$ : a first value of  $q$  is calculated which gives  $K_1$ , and, using the preceding relations with  $K = K_1$ , the number of entities  $N_{1\text{Pu(X)}}$  in the transient equilibrium is found. This procedure yields a new average value  $q_1$  of the ratio, and consequently a new value

for  $K$ , i.e.  $K_2$ . Next, a new set  $K_2$  and  $N_2$  is chosen, in which  $N_2$ , which is immediately below  $N$ , is the integer value of the sum of the average number of the  $N_{2\text{Pu(X)}}$  entities calculated with  $K_2$ , and so on. It is seen that the equilibrium constant decreases from its initial value to that allowed by the smallest value of  $N$  compatible with the stoichiometry of the reaction.

Fig. 5 shows that for  $K < 1$ , the  $q$  values drop very rapidly as  $N$  decreases. This means that less and less Pu(V) atoms disproportionate when the population diminishes. The situation is the same when  $K > 1$ , but now chaotic discontinuities may appear in the evolution of  $q$  when the successive  $N$  values suddenly change from an even to an odd series and conversely. This case should be compared to that of Fig. 4.

### 5. Are the prognosticated reactions observable?

As a last point, the conditions for measurement of the equilibrium state at the sub-tracer level should be defined. The number of radionuclides necessary for registering an activity of one disintegration per min is related to the half-life  $T$  (s) by

$$T = 42N$$

which gives  $N = 1.5 \times 10^{10}$  atoms for fall-out Pu or  $6 \times 10^7$  atoms for  $^{238}\text{Pu}$ . The detection of 100 atoms of Pu by  $\alpha$  counting is beyond the reach of the most sensitive solid-state detectors and the best available measuring conditions. Even the detection of one  $\alpha$  particle per day above background in the 5.5 MeV energy range would not be sufficient. It must be concluded that the establishment of equilibria involving Pu in a large closed system has little chance of being confirmed, although chemical separation methods of Pu in its various oxidation states are known [15, 45–46]. A better approach might lie in the analysis of a large number of very small closed systems or in the use of new and improved methods. Laser resonance ionization mass spectrometry reputedly permits detection of the order of  $10^7$  atoms [47]. But even in this case, the experimentalist is still faced with the problem of dealing with numbers of atoms that are smaller by many orders of magnitude.

### 6. Conclusion

The arguments developed here have little practical importance with respect to the environmental chemistry of Pu and may appear somewhat fictitious. Perhaps a more appropriate title for this discussion would have been "Speculative Pu chemistry at very low concentration". Nevertheless, reflexions on the chemistry of Pu provide an opportunity for examining more general questions on the behaviour of highly diluted matter. Even if the problem can be treated by appropriate theoretical argumentation, conclusions derived from reactions between microcomponents cannot be checked experimentally owing to the necessity of con-

collating three conditions, of which two are opposed. the artificial radionuclide should possess several oxidation states and a half-life short enough (say 1 min) to facilitate the detection of a few atoms, but simultaneously long enough to allow for completion of the equilibrium, which may require hundreds of years! Unfortunately, Pu isotopes, fulfill only two of these three conditions.

### Acknowledgments

The authors thank P. Vitorge, H. Capdevila and V. Moulin for helpful discussions and for providing up-to-date data. P. Delamoye is thanked for the computation of  $q$  values.

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